

evaporation is always more encumbered, partly, no doubt, because its evaporating surface is a fixture. The only limit to the rise of temperature of a liquid is its boiling, but if this be prevented it may get superheated; and, unless the solid boil (*i.e.* disintegrate internally) it can become superheated to any extent. The possibility of this internal disintegration we will examine directly, but at present we will consider it practically *nil*.

Let us grant then that a subliming solid always rises in temperature if heated at a sufficient rate, and Dr. Carnelley's proposition follows.

We have seen that no liquid can exist at temperatures below its freezing- or above its boiling-point, so that if we wish to prevent the possibility of its existence, we need only make these two points coincide. This can always be done by diminishing the pressure, for the boiling-point of all substances is greatly affected by changes of pressure, while the freezing-point is only slightly altered, and even, in the case of ice, in the opposite direction.

Start then with the solid below its melting-point, and reduce the pressure on it till the boiling-point coincides with, or passes below the melting-point. There is now no region where liquid can exist, and the solid must therefore sublime; but, by our supposition, a subliming solid if heated will get hot, hence the solid may now assume any temperature you please; and the hotter it gets the more pressure may be brought to bear upon it without causing it to melt, *i.e.* the pressure may be allowed to increase to anything short of the vapour-tension at the new temperature. If heated sufficiently, then the whole atmospheric pressure may be let in, and no melting will occur. All that is necessary is that heat shall be supplied at a sufficient rate to compensate for the rapid evaporation (which however will not be so rapid as in the vacuum), and to prevent its temperature falling to the boiling-point; for if it reached this, part (or all) would quickly liquefy, and the whole fall to (or towards) the melting-point.

Thus we have the remarkable proposition that if, by the process of lowering the boiling-point to coincide with or pass below the melting-point, we manage to get ice across the gap which ordinarily separates these two points, it may be heated to 120° or to any other temperature; and that when at 120° it will be permanent, and will not melt even under the whole pressure of the atmosphere. To prevent its melting you must keep on heating it: if allowed to cool to 100°, five-eighths of it will be instantly crushed to water, and the whole will be at 0° (assuming, what is not likely to be correct, that the specific heat of hot ice is $\frac{1}{2}$).

There is still the question of the possibility of internal melting or sublimation to be considered.

Now I suppose that if a solid is perfectly homogeneous, a change of state in its interior would with great difficulty occur, and the solid might readily be superheated. But an excess of pressure at any point, such as would be produced by a bubble of air, would readily determine a melting-centre. In Prof. Tyndall's ice-flower experiment the nuclei are probably minute bubbles of air, and the ice walls of the cavities so produced are subject to the pressure of this air in addition to that of the vapour; and accordingly melting sets in and spreads. But Dr. Carnelley's ice is formed *in vacuo*, so that no air-bubbles are possible, and the only nuclei that can properly exist are little bubbles of enclosed vapour; and these, I imagine, can scarcely be absent. Let us inquire then what can happen in the case of one of these bubbles when the temperature of the ice is raised either by radiation or conduction. Initially, while the temperature is constant, the vapour is saturated; but no liquid is formed because this temperature is below the melting-point. When heat is applied, the ice, being less diathermanous than the vapour, will get heated first, and so long as the temperature keeps rising it will always be a little hotter than the vapour, which consequently is not quite saturated, and the pressure it exerts is less than the "vapour-tension" (*i.e.* the temperature is above the boiling-point), and no water can be formed. The cavity will of course enlarge by sublimation, but very slowly, much more slowly in fact than outside, if a vacuum is there artificially maintained.

But if cooling be permitted the ice will cool the fastest; and the vapour at once becomes over-saturated and condenses. The temperature is now below the boiling-point, and liquefaction instantly sets in and rapidly spreads, the ice consuming its own heat in the process.

Internal disintegration therefore will not occur while the temperature is rising, but it will set in at a great pace if it be allowed

to become stationary or to fall, unless there be an utter absence of nuclei. If the temperature rises very high the pressure of the internal vapour will of course be great, and ultimately might even be able to burst the ice, but this would scarcely occur under several atmospheres.

It would be interesting if Dr. Carnelley would kindly try the following experiments:—

1. Heat ice *in vacuo* with a pressure gauge, and, still heating it, stop the passage to the condenser so that the pressure is allowed to accumulate, and note the pressure and temperature when collapse occurs.

2. Heat ice up to any temperature, and, still maintaining a good vacuum, remove the supply of heat, and see if the ice does not collapse.

3. Heat the ice up to 120°, and, still heating it, let in the atmosphere gently (but make the air come in through hot pipes, or it will melt the ice), and see if the ice does not last rather longer than it would have done in the vacuum, because the evaporation will be more obstructed. But if the second experiment succeed, the temperature must never be allowed to fall much or to remain stationary long.

Finally, it is important to point out explicitly that the Carnelley experiment has no bearing on the change of the melting-point of ice with pressure. Our knowledge on this point remains as it was, viz.

that the value of $\frac{d\theta}{dp}$ about zero centigrade is $-.0071$; that is to

say, the melting-point rises and falls about $.0071^\circ$ centigrade per atmosphere of pressure decrease or increase.

Of course this number is not absolutely constant, but its variation with pressure is very slight, and moreover has no bearing on the Carnelley experiment, as was naturally but erroneously supposed by Prof. Pettersson in the *Berichte* (18), and I believe also by Prof. Ayrton at the Chemical Society, though I had not the pleasure of hearing his remarks.

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Note.—With reference to the above second experiment and the reasoning which suggested it, it is important to remark that I have all along assumed that the vapour-tension of ice at any temperature is precisely the same as that of water at the same temperature. But Prof. Foster considers it possible that the vapour-tension of ice may be less than that of water, and would hence explain the permanence of vapour inside an ice-cavity without attending to whether the temperature were rising or falling, provided it were not falling too fast. This would be a most important fact to discover and verify; but I think the Carnelley experiment in its present form does not inform us concerning its truth or falsity.

Another thing it may be interesting to note is the rate of variation of boiling-point with pressure at different temperatures, which can be calculated on thermodynamic principles (after Prof. James Thomson) from empirical data for the latent heat of steam, and for the density of saturated steam at any temperature.

It is, at the temperature θ and the pressure p ,—

$$\frac{d\theta}{dp} = \frac{\theta^2}{273 \times .008 \times (796.2 - .695\theta) J p'}$$

a fraction which has the value 28 at 100° C., and 2180 at 0° C.: these numbers represent the rate of rise or fall of boiling-point in centigrade degrees per atmosphere increase or decrease.

Integrating this equation, we get the value of the vapour-tension p of water in atmospheres (megadynes per square centimetre) at any absolute temperature θ , viz:—

$$\log p = 9.1728 \left\{ .695 \log \frac{373}{\theta} + 796.2 \left(\frac{1}{373} - \frac{1}{\theta} \right) \right\},$$

the logarithms being to the base e .

On the Spectrum of Carbon

I HAVE a great respect for Dr. Watts's spectroscopic work, nevertheless the experiments he has described in *NATURE*, vol. xxiii. p. 197, appear to me singularly inconclusive for the purpose for which he has adduced them. How could any one expect to get a tube of gas free from hydrocarbons when the joints were of india rubber and melted paraffin? I have long since found it necessary to forego rubber joints if I would exclude hydrogen. Salet has shown that the hydrocarbons from the blowpipe-flame used in sealing in wires, &c., and the last traces of dust, can only be removed from tubes by burning them out in a current of oxygen. But more than this, I have found

that even with joints all made by fusion of the glass it was well nigh impossible to get rid entirely of hydrogen. Mr. Crookes has, I believe, found that the last traces of moisture adhering to glass can only be expelled by heating to the softening point of the glass. This tallies with my own experience. In a series of experiments on the ultra-violet water spectrum I had occasion to photograph the spectra of sparks in sundry gases wet and dry, and found that in gases which had been passed through a tube full of phosphoric anhydride the water-spectrum still appeared strongly. Even when the gas had been passed very slowly through two tubes each half a meter long filled with calcium chloride, and then through a similar tube full of phosphoric anhydride, and the part of the tube where the wires were sealed had been heated strongly for a long time, while the current of gas was passing, traces of the water spectrum still often appeared. But Dr. Watts did not see the hydrogen lines in his tube. My difficulty has always been to avoid seeing them when the pressure of the gas was sufficiently reduced and a large condenser used with the induction coil. True: tubes of gas may not always show them even when hydrogen is known to be present. The spark takes a selected course of its own, and does not always light up all that is in the tube. Carbonic oxide does not generally show oxygen lines, and in tubes exhausted by a Sprengel pump the lines of mercury do not usually appear until the pumping has been carried far. A real test would be to see whether when the spark gives the line-spectrum of carbon the hydrogen lines do not also appear. The experiment with naphthaline Prof. Dewar and I have repeated and discussed elsewhere, so I will say no more on it than this, that purity in regard to chemicals is a relative rather than an absolute quality, and that it is only from a long series of experiments chosen with a view to eliminate the effects of accidents of all kinds that any safe induction in this kind of spectroscopy can be reached.

Cambridge, January 4

G. D. LIVEING

[To save time we submitted Prof. Liveing's letter to Mr. Watts, who sends the following reply.—Ed.]

I SEE no reason why india-rubber stoppers may not be used in the construction of an apparatus to be filled with a gas at atmospheric pressure, or nearly so. The case would be altogether different if we were concerned with the construction of a vacuum tube, and I take it that most of these statements of the difficulty of getting rid of the last traces of moisture and of hydrocarbons adhering to the glass refer to cases where the pressure is to be only a few millimetres. But when a current of cyanogen at atmospheric pressure, made from dried mercuric cyanide, is passed through a U-tube filled with phosphoric anhydride, the gas is surely dry to all intents and purposes (I do not say that the glass would not give off traces of moisture, &c., if the pressure were to be reduced to an extreme point); at least there can be so little hydrogen present in the tube that to ascribe the spectrum given by the tube to the hydrogen present in it is to adopt an extreme hypothesis, which must be supported by cogent experimental evidence before it can be accepted.

But if the defect of the experiment be in the use of india-rubber there can be no great difficulty in constructing the apparatus entirely of glass, and if we are to give up the view that the groups δ (5165 to 5082) and γ (5635 to 5478) are due to carbon, it must be shown that they are not present in the spectrum of the spark in cyanogen at atmospheric pressure when sufficient precautions are taken to obtain the gas pure. I have never examined the spectrum of the spark in cyanogen without seeing them, and have every confidence that Prof. Liveing will still find them there after he has taken all the precautions he may think necessary.

But admitting for the sake of argument the justice of Prof. Liveing's contention that the cyanogen in my experiment contained a trace of hydrogen and that the naphthalin contained a trace of nitrogen, then this seems to be the theory offered for our acceptance—that the spark in nitrocarbon gas containing a trace of hydrogen gives the lines of hydrocarbon, and that the spark in hydrocarbon gas containing a trace of nitrogen gives the lines of nitrocarbon. Does Prof. Liveing hold *both* of these hypotheses to be reasonable?

W. M. WATTS

Geological Climates

THE letter of Prof. Haughton in last week's NATURE so bristles with figures and calculations that some of your readers

may feel a little puzzled and may be unable to detect the fallacies that lurk among them. The question is far too large a one to be fully discussed in your columns. I shall therefore confine myself to pointing out the erroneous assumptions and false inferences which vitiate all the learned Professor's calculations, having done which my own theory will remain, so far, intact.

The whole argument against me is based upon an "ideal ice-cap," extending from the Pole to lat. 60°. A considerable but unknown thickness is given to this imaginary field of ice, and it is then calculated that the three great ocean streams, even if admitted to the Arctic area in the manner I suggest, would not get rid of this mass of ice. There are however several important misconceptions and illogical deductions underlying the whole argument, and when these are exposed the results, however accurately worked out, become completely valueless.

We first have it stated that if heat and cold were uniformly distributed over the Polar regions the whole would be permanently frozen over, and an ice-cap be formed of great but varying thickness, diminishing from the Pole to about lat. 60°. But even this preliminary statement is open to serious doubt; for ice cannot be formed without an adequate supply of water, and over a large part of the Polar area no more snow falls than is annually melted by the sun and by warm southerly winds blowing over the heated land-surfaces of Asia and America. Admitting however that any such ice-cap could be formed, it would certainly not form in *one year* but by the accumulations of a long series of years; and any estimate of the *total* heat required to melt it has no bearing whatever on the *annual* amount that would be sufficient, since this depends solely on the average thickness of the ice *annually* formed, of which Prof. Haughton says nothing whatever.

The amount of rainfall in the Arctic regions (mostly in the form of snow) is certainly very small. It is estimated by Dr. Rink to be only twelve inches in Greenland, and this is probably far above the average. All that falls on the inland plains of Asia, Europe, and America is however melted or evaporated by the action of the sun and air far from the influence of the Gulf Stream. The thickness of ice formed annually over the whole area of the Arctic Ocean I have no means of estimating. In open water in very high latitudes it may be considerable, but perennial ice-fields can only increase very slowly. I should therefore very much doubt if the thickness of ice now formed annually over the whole Arctic area averages nearly so much as five feet; and Prof. Haughton himself calculates that our own Gulf Stream is now capable of melting this quantity.

The first assumption, therefore—that the amount of heat required to be introduced into the Arctic regions in order to raise their mean temperature above the freezing-point is "accurately measured" by the amount required to melt an "ice-cap" covering the whole area to a thickness of several hundred feet—is grossly erroneous; and it is so because it takes the hypothetical *accumulated* effects of *many years* Arctic cold under altogether impossible conditions, and then estimates the amount of heat required to melt this whole accumulation in *one year*!

But we find a second and equally important error, in the assumption (involved in all Prof. Haughton's arguments and figures) that all the ice of the alleged "ideal ice-cap" must be melted by that portion of the Gulf Stream which actually enters the Polar area, where its temperature is taken to be 35° F. or only 3° above the melting point of ice. A large quantity of the Arctic ice, however, even now floats southward to beyond lat. 50° in both the Atlantic and Pacific, and is melted by the warmer water and atmosphere and the hotter sun of these lower latitudes. Now, as it is an essential part of my theory that much of Northern Asia and North America were under water at those early periods when warm climates prevailed in the Arctic regions, it is clear that whatever Arctic ice was then formed would have a freer passage southwards, and as the south-flowing return currents would then have been more powerful and more extensive than at present, a much larger proportion of the ice would have been melted by the heat of temperate instead of by that of Arctic seas.

Prof. Haughton admits that the Kuro Siwo and the Mozambique currents together, if they entered the Polar seas, would be equal to the melting of a layer of ice more than thirteen feet thick over the whole area down to lat. 70°. But if our own Gulf Stream is sufficient to get rid of the whole of the ice that now forms annually—as Prof. Haughton's figures show that it would probably be, and as it would be still more certainly were Greenland depressed, thus ceasing to be the great Arctic refrigerator and ice accumulator—then the heat of the other two currents would be employed in raising the temperature of the Arctic seas above